

*February 22, 1894.*

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Bakerian Lecture was delivered as follows:—

BAKERIAN LECTURE.—“On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature.” By T. E. THORPE, D.Sc., F.R.S., and J. W. RODGER, Assoc. R.C.S. Received February 22, 1894.

(Abstract.)

The purpose of this paper is to throw light upon the relations between the viscosity of homogeneous liquids and their chemical nature. It is divided into three parts.

Part I contains a summary of the attempts which have been made, more particularly by Poiseuille, Graham, Rellstab, Guerout, Pribram and Handl, and Gartenmeister, to elucidate this question. Although it is evident from the investigations of these physicists that relationships of the kind under consideration do exist, it must be admitted that they are as yet not very precisely defined, mainly for the reason that the conditions by which truly comparable results can alone be obtained have received but scant consideration.

For example, it seems futile to expect that any definite stoichiometric relations would become evident by comparing observations taken at one and the same temperature. Practically, nothing is known of a quantitative character concerning the influence of temperature on viscosity.

From the time which a liquid takes to flow through a capillary tube under certain conditions, which are set out at length in the paper, a measure of the viscosity of the liquid can be obtained.

An apparatus was, therefore, designed on this principle which admitted of the determination in absolute measure of the viscosity, and for a temperature range extending from 0° up to the ordinary boiling point of the liquid examined. In this way instead of finding, as has been the usual custom, relative times of flow in the same apparatus under the same external conditions of temperature and pressure, and which

might or might not be taken as measures of a single physical magnitude of the substance, *i.e.*, its viscosity, the physical magnitude itself could be measured, and the various influences which are found to affect its value could be allowed for. The physical constants thus obtained could then be treated from the point of view of the chemist, and the comparison would then be of the same kind as that employed in connexion with other physical magnitudes.

Full details of the conditions determining the dimensions of the apparatus and of the modes of estimating these dimensions, together with the methods of conducting the observations, are given in the paper.

The corrections to be applied to the direct results are then discussed.

The question of the mathematical expression of the relation of viscosity of liquids to temperature is considered, and reasons are given for preferring the formula of Slotte—

$$\eta = c/(1+bt)^n,$$

$\eta$  is here the coefficient of viscosity in dynes per square centimetre, and  $c$ ,  $b$ , and  $n$  are constants varying with the liquid.

With a view of testing the conclusions set out at length in the historical section of the paper, and, in particular, of tracing the influence of homology, substitution, isomerism, and, generally speaking, of changes in the composition and constitution of chemical compounds upon viscosity, a scheme of work was arranged which involved the determination, in absolute measure, of the viscosity of some seventy liquids, at all temperatures between  $0^\circ$  (except where the liquid solidified at that temperature) and their respective boiling points.

Part II of the memoir is concerned with the origin and modes of establishing the purity of the several liquids; it contains the details of the measurements of the viscosity coefficients, together with the data required to express the relation of viscosity coefficients to temperature by means of Slotte's formula, and tables are given showing the agreement between the observed and calculated values.

In Part III the results are discussed. In the outset the factors upon which the magnitude of the viscosity probably depends are dealt with. The influence of possible molecular aggregations, as indicated by observations of vapour densities, boiling points, and critical densities, and, more especially, by measurements of surface energy, made by Eötvös in 1886, and more recently by Ramsay and Shields, are taken note of.

The deductions which may be made by considering the graphical representation of the results, showing the variations of viscosity coefficients with temperature, are then set forth.

For liquids which probably contain simple molecules, or for which

there is little evidence of association of molecules at any temperature, the following conclusions may be drawn:—

1. In homologous series the coefficient of viscosity is greater, the greater the molecular weight.

2. An iso-compound has always a smaller viscosity coefficient than the corresponding normal compound.

3. An allyl compound has, in general, a coefficient which is greater than that of the corresponding isopropyl compound, but less than that of the normal propyl compound.

4. Substitution of halogen for hydrogen raises the viscosity coefficient by an amount which is greater, the greater the atomic weight of the halogen; successive substitutions of hydrogen by chlorine in the same molecule bring about different increments in the viscosity coefficients.

5. In some cases, as in those of the dichlorethanes, substitution exerts a marked influence on the viscosity, and in the case of the dibromides and benzene, it may be so large that the compound of higher molecular weight has the smaller viscosity.

6. Certain liquids, which probably contain molecular complexes, do not obey these rules. Formic and acetic acids are exceptions to Rule 1. The alcohols at some temperatures, but not at all, are exceptions to Rule 2; at no temperatures do they conform to Rule 3.

7. Liquids containing molecular complexes have, in general, large values of  $d\eta/dt$ .

8. In both classes of liquids the behaviour of the initial members of homologous series, such as formic acid and benzene, is in some cases exceptional when compared with that of higher homologues.

As regards the influence of temperature on viscosity, it is found that the best results given by Slotte's formula are in cases where the slope of the curve varies but little with the temperature. From the mode in which the values of the constants  $n$  and  $b$  are derived, it cannot be expected that their magnitudes will be related in any simple manner to chemical nature. With the exception of certain liquids, such as water and the alcohols, which are characterised by large temperature coefficients, and in which there is reason to expect the existence of molecular aggregates, the formula

$$\eta = c/(1 + \beta t + \gamma t^2),$$

obtained from Slotte's expression by neglecting terms in the denominator involving higher powers of  $t$  than  $t^2$ , gives a close agreement with the observed results, and in this formula the magnitude of  $\beta$  and  $\gamma$  are definitely related to the chemical nature of the substances.

In order to obtain quantitative relationships between viscosity and

chemical nature, and to compare one group of substances with another, it is necessary to fix upon particular temperatures at which the liquids may be taken as being in comparable conditions as regards viscosity, and to compare the values of the viscosities at those temperatures.

The first comparable temperature which suggested itself was the boiling point.

A second comparable temperature was obtained by calculating values of corresponding temperatures by the method of van der Waals with such data as could be obtained.

The third basis of comparison consisted in using temperatures of equal slope, *i.e.*, temperatures at which the rate of change of the viscosity coefficient is the same for all liquids.

At each of the different conditions of comparisons, the experimental results have been expressed according to the same system, in order to show at a glance relationships between the magnitudes of the viscosity constants and the chemical nature of the substances. The liquids are arranged so that chemically related substances are grouped together. Tables are constructed which give the values of the three different magnitudes derivable from measurements of the viscosity of the substances.

1. Values of viscosity coefficients ( $\eta$ ).
2. Values of  $\eta \times$  molecular area, *i.e.*, *molecular viscosity*.
3. Values of  $\eta \times$  molecular volume, *i.e.*, *molecular viscosity work*.

The coefficient  $\eta$  is the force in dynes which has to be exerted per unit-area of a liquid surface in order to maintain its velocity relative to that of another parallel surface at unit distance equal to unity. It seemed, however, that relations between viscosity and chemical nature would best be brought to light if, instead of adopting merely unit-areas, areas were selected upon which there might be assumed to be the same number of molecules. The *molecular viscosity* is proportional to the force exerted on a liquid molecule in order to maintain its velocity equal to unity under the unit conditions above defined. With the units chosen it is the force in dynes exerted on the molecular area in square centimetres under unit conditions. The *molecular viscosity work* may be regarded as proportional to the work spent in moving a molecule through the average distance between two adjacent molecules under unit conditions. In ordinary units it is the work in ergs required to move a surface equal to the molecular area in square centimetres through the molecular length in centimetres.

In the case of the comparison of the viscosity coefficients at the boiling point, it is found :

1. As an homologous series is ascended, in a few cases the viscosity coefficient remains practically the same, but in the greater number of series the coefficients diminish. In one series the coefficients increase ;

in the case of the alcohols the coefficients vary irregularly with ascent of the series.

2. Of corresponding compounds, the one having the highest molecular weight has in general the highest coefficient (the aliphatic acids, and to a much greater extent the alcohols, do not conform with this rule).

3. Normal propyl compounds have, as a rule, slightly higher values than allyl compounds; in the case of the alcohols, propyl compounds have much the higher value.

4. The effect of molecular weight in some cases may be more than counterbalanced by that of constitution, or of complexity.

5. The lowest members of homologous series frequently exhibit deviations from the regularity shown by higher members.

6. An iso-compound has in general a larger coefficient than a normal compound, and the differences reach their maximum in the case of the alcohols.

7. In the case of other metameric substances, branching in the atomic chain and the symmetry of the molecule influence the magnitudes of the coefficients; the ortho-position, in the case of aromatic compounds, appears to have a more marked effect on the coefficient than either the meta- or para-position. Acetone and ether have coefficients that are less than half the values given by the isomeric alcohols.

8. One of the most striking points thus brought to light is the peculiar behaviour of the alcohols, and to some extent of the acids, as contrasted with that of other liquids.

Comparisons of molecular viscosity at the boiling point show—

1. That, with the exception of the alcohols, dibromides, and the lowest members of homologous series, an increment of  $\text{CH}_2$  in chemical composition corresponds with an increase in molecular viscosity.

2. With the above exceptions, it is also apparent that the corresponding compound having the highest molecular weight has the highest molecular viscosity: the difference in molecular viscosity between the corresponding members of two correlated series is fairly constant.

3. The relationships shown in the other tables are substantially of the same nature as those given by the viscosity coefficients.

The comparisons which give the largest deviation from regularity contain those substances which, as already shown, exhibit a peculiar behaviour, namely, the alcohols, acids, propylene dibromide, ethylene dichloride, &c.

In order to indicate how molecular viscosity at the boiling point is quantitatively connected with chemical nature, attempts were made to calculate the probable partial effects of the atoms on the molecular

viscosity. Values were also assigned to the effects of the iso-grouping of atoms, the double linkage of carbon atoms, and the ring grouping. The values thus obtained are given in the following table :—

Fundamental Viscosity Constants (molecular viscosity at the boiling point, in dynes  $\times 10^4$ ).

Hydrogen.....	80
Carbon.....	—98
Hydroxyl oxygen, C—O—H .....	196
Ether oxygen, C—O—C .....	35
Carbonyl oxygen, C=O.....	248
Sulphur, C—S—C .....	155
Chlorine.....	284
Bromine (in monobromides) .....	420
Bromine (in dibromides) .....	479
Iodine .....	520
Iso-grouping .....	15
Double-linkage .....	113
Ring-grouping.....	610

As regards the meaning to be attached to fundamental viscosity constants in general, the following points may be noted. Viscosity may be taken as a measure of the attractive forces in play between molecules, *i.e.*, of intermolecular attraction. From the fact that an increment of  $\text{CH}_2$  in chemical composition, or the substitution of an atom of chlorine, bromine, or iodine for an atom of hydrogen, brings about a definite change in the viscosity, it is evident that intermolecular attraction is really a property of the atoms forming molecules. But, besides change in molecular weight, change in the mode of grouping of the same atoms also affects the magnitude of the viscosity. The observations show that iso-compounds have values differing from those of isomeric normal compounds; ring compounds have not the values which, by the study of straight chain compounds, they might be expected to have. Compounds containing hydroxyl oxygen give values of the viscosity differing widely from those of compounds containing carbonyl oxygen. The same atoms must, therefore, exert different effects when differently linked together. That the effects of all the atoms in the molecule are not altered by change in the mode of linkage is proved by the fact that the effect of  $\text{CH}_2$ , of iodine, of bromine, &c., is the same in normal and in iso-compounds.

In the present state of the question it is impossible to say what particular atoms are affected by change in the mode of linkage. Hence the method adopted in deducing fundamental constants is to assume that certain atoms retain the same values under all conditions,

whilst the change in the values of those atoms which are affected by the mode of linkage is, when possible, expressed either by a new constant—the value of an iso-linkage, a double linkage, &c., or by saying that a particular atom has assumed a new value, *e.g.*, carbonyl oxygen, hydroxyl oxygen, &c. In some cases the method of calculation may lead to the result that a negative constant is ascribed to a particular atom. In deducing the values of carbon and hydrogen, for example, it is implied that in a  $\text{CH}_2$  group and in the molecule of a paraffin the individual effect of each atom of carbon or of hydrogen is the same. The above facts, and the reasoning based upon them, show that this is not the case, and although the absolute effect exerted by each atom upon the viscosity is positive, the fundamental constant of an atom may be negative, as it may involve a constitutive effect, which at present cannot be localised in a particular region of the molecule. For these reasons fundamental constants are to be regarded as empirically ascertained magnitudes, which are merely intended to indicate how far the observed results may be represented as the sum of partial values which are the same for all substances. They have no reference to the possible behaviour of the elements when in the free state; they simply show how far definite changes in chemical nature correspond with definite changes in viscosity.

Tables are given which show the concordance between the observed molecular viscosity and those calculated by means of these constants. In the case of forty-five liquids the difference between the observed and calculated values rarely exceeds 5 per cent. In the case of the isomeric ketones and aromatic hydrocarbons, the differences are in part due to constitutive influences, which cannot at present be allowed for in obtaining the calculated values.

In a second table are given those substances for which the differences exceed this 5 per cent. limit. These may be roughly classed as unsaturated hydrocarbons, polyhalogen compounds, formic and acetic acids, benzene, water, and the alcohols.

Similar fundamental constants for molecular viscosity work at the boiling point have also been deduced. These are given in the table on p. 155.

Tables are also given showing the comparison between the observed and calculated numbers, the substances being classified into two groups, as in the case of molecular viscosity, according as the differences are less or greater than about 5 per cent.

On taking a general survey of the comparisons at the boiling point, it is evident that for the majority of the substances examined—the paraffins and their monohalogen derivatives, the sulphides, the ketones, the oxides, and most of the acids and the aromatic hydrocarbons—molecular viscosity and molecular viscosity work may be

Fundamental Viscosity Constants (molecular viscosity work at the boiling point, in ergs  $\times 10^3$ ).

Hydrogen.....	-1.5
Carbon .....	50
Hydroxyl oxygen, C—O—H.....	102
Ether oxygen, C—O—C.....	27
Carbonyl oxygen, C=O.....	41
Sulphur, C—S—C .....	99
Chlorine .....	109
Bromine (in monobromides).....	176
Bromine (in dibromides) .....	212
Iodine .....	233
Iso-grouping .....	5
Double-linkage .....	31
Ring-grouping.....	60

quantitatively connected with chemical nature. The remaining substances—unsaturated hydrocarbons, di- and poly-halogen compounds, formic acid, benzene, water, and the alcohols—present marked exceptions to the foregoing regularities.

As regards the comparison of the viscosity magnitudes at the corresponding temperature, it is found that, although the critical data are too unsatisfactory to warrant us in laying any particular stress on the relationships obtained under this condition of comparison, these relationships are similar to, even if less definite than, those obtained at the boiling point. For a property like viscosity, which alters so rapidly with temperature, a corresponding temperature is no better as a condition of comparison than the boiling point.

On comparing the viscosity curves of those substances which give the best physicochemical relationships at the boiling point, it was at once seen that the general shape of the curves towards the boiling point was practically the same. If tangents were drawn to the curves at points corresponding with the boiling points of the liquids, the inclinations of the tangents to the axes, that is, the *slopes* of the curves, varied but little. On the other hand, the curves for liquids such as the alcohols, or the lowest members of homologous series, which gave little indication of physicochemical relationships, had invariably a different shape; the inclinations of tangents drawn at the boiling point were markedly different from those of the majority of substances. It seemed probable, therefore, that the discrepancies were related to this difference in the value of the slopes, and that, if the temperature of comparison was chosen so as to eliminate this difference, better relationships ought to be obtained. This idea led



to the adoption of temperatures of equal slope as comparable temperatures, and, indeed, apart altogether from considerations such as the above, which refer to the particular case of viscosity, much may be said, from a theoretical point of view, in favour of employing such temperatures for physicochemical comparisons in general.

To begin with, at the temperature of equal slope, the effect of temperature upon the property examined is the same for different substances. In the case of viscosity, for instance,  $d\eta/dt$ , or the rate at which viscosity is being altered by the temperature, has the same value for all liquids, and this equality might be taken as sufficient justification for supposing that at temperatures of equal slope the substances, so far as viscosity is concerned, are in comparable states.

Another argument which may be advanced in favour of such a method of treatment is that the comparable temperatures are chosen by means of a study of the effect of temperature on the property actually examined. The main objection which can be urged against the boiling point as a comparable temperature, even when, as in the case of such a property as density, it gives comparatively definite stoichiometric relationships, is that these relationships may not be general. If, however, comparable temperatures be chosen, as in the case of slope by a study of the property considered, the generality of the relationships obtained can be ascertained without the study of other properties of the substances.

Comparisons were made, therefore, at temperatures at which  $d\eta/dt$  is the same for the different liquids. Or, graphically, the temperatures may be defined as those corresponding with points on the viscosity curves at which tangents are equally inclined to the axes of co-ordinates. The temperatures are therefore those at which temperature is exercising the same effect on viscosity, and for shortness may be termed *temperatures of equal slope*. The temperatures were obtained by means of Slotte's formula.

It was apparent from the shape of the curves that all the liquids could not be compared at any one value of the slope, because the effect of temperature on the slope varied so much from substance to substance. In some cases—the whole of the alcohols for example—the slope at the boiling-point was considerably greater than that at  $0^\circ$  in the case of some of the less viscous liquids. A slope was, therefore, selected at which as many liquids as possible could be compared. Another slope was then obtained at which the outstanding liquids could be compared with as many as possible of the liquids used at the original value of the slope. The relationships between the magnitudes of the viscosities of these liquids which could be compared at the two slopes were then found to be *the same at either slope*, so that general conclusions regarding the behaviour of all the liquids could be deduced. These are as follows:—

1. Temperatures of equal slope tend to reveal much more definite relationships between the values of viscosity coefficients and the chemical nature of the substances than are obtained at the boiling point.

2. In all homologous series, with the exception of those of the alcohols, acids, and dichlorides, the effect of  $\text{CH}_2$  on the value of the coefficient is positive, and tends to diminish as the series is ascended.

3. Of corresponding compounds the one of highest molecular weight has the highest coefficient.

4. Normal propyl compounds have slightly larger coefficients than the corresponding allyl compounds.

5. An iso-compound has invariably a larger coefficient than a normal compound.

6. In the case of other isomers the orientation of the molecule and branching of the atomic chain influence the magnitudes of the coefficients. Similar effects of constitution are also exhibited on comparing saturated and unsaturated hydrocarbons, and the variable effects produced by successive substitution of halogen for hydrogen.

7. The alcohols, and to some extent the acids, still give results which are peculiar when compared with other substances.

As regards molecular viscosity at equal slope the following conclusions may be drawn:—

1. For the great majority of the substances molecular viscosity at equal slope can be calculated from fundamental constants which express not only the partial effects of the atoms existing in the molecule, but also those due to different atomic arrangements. These are given in the accompanying table:—

Fundamental Viscosity Constants (molecular viscosity at Slope  $0.0,323$ , in dynes  $\times 10^4$ ).

Hydrogen.....	44.5
Carbon .....	31
Hydroxyl oxygen, $\text{C—O—H}$ .....	166
Ether oxygen, $\text{C—O—C}$ .....	58
Carbonyl oxygen, $\text{C=O}$ .....	198
Sulphur, $\text{C—S—C}$ .....	246
Chlorine (in monochlorides).....	256
Chlorine (in dichlorides).....	244
Bromine (in monobromides).....	372
Bromine (in dibromides).....	361
Iodine.....	499
Iso-grouping .....	— 21
Double-linkage.....	48
Ring-grouping.....	244

The large effects which can be attributed to the ring-grouping of atoms, to the iso-linkage, to double-linkage, and to changes in the condition of oxygen in its compounds, as well as the smaller effects due to the accumulation of atoms of halogen in a molecule, render evident the quantitative influence of constitution.

2. Of the remaining substances the chlormethanes, tetrachlor-ethylene, ethylidene chloride and carbon bisulphide give deviations from the calculated values on account of constitutive influences not allowed for in obtaining the fundamental constants.

3. The alcohols and water exhibit no agreement with the calculated values. The mode in which deviations vary indicates, in the case of the alcohols, that the disturbing factor is related to their chemical nature.

The results obtained from the consideration of molecular viscosity work at equal slope, are of precisely the same nature as those discussed under molecular viscosity.

The fundamental constants are as follows:—

Fundamental Viscosity Constants (molecular viscosity work at Slope 0.04323, in ergs  $\times 10^3$ ).

Hydrogen.....	— 34
Carbon .....	148
Hydroxyl oxygen, C—O—H.....	100
Ether oxygen, C—O—C .....	43
Carbonyl oxygen, C=O.....	— 19
Sulphur, C—S—C .....	144
Chlorine (in monochlorides) .....	89
Chlorine (in dichlorides).....	82
Bromine (in monobromides) .....	151
Bromine (in dibromides).....	148
Iodine.....	218
Iso-grouping .....	— 8
Double-linkage .....	— 95
Ring-grouping.....	—369

The substances which give deviations from the calculated values fall into two classes. In the first the deviations are to be attributed to chemical constitution, inasmuch as similar disturbing effects may be detected in the magnitudes of other physical properties which afford no evidence of being influenced by molecular complexity.

In the second are substances like the acids, water, and the alcohols, for which the disturbing factor is, no doubt, molecular complexity.

The question of the generality of the results obtained is next discussed. It is evident :

1. That over such temperature ranges as the observations extend the results obtained at a particular value of the slope may be regarded as general for all liquids, with the exception of the alcohols, for which the relationships vary slightly as the slope alters. A general expression connecting the viscosity coefficient with the slope is given.

2. It is further indicated, from comparisons made by the use of slopes which varied from liquid to liquid, and which were chosen according to definite systems, that in the present state of the question equal slope is the most suitable condition at which to compare the viscosities of different liquids.

With respect to the relationships existing between the magnitudes of the comparable temperatures of equal slope, it appears:—

1. That these vary in a regular way with the chemical nature of the substances, except in the case of liquids like benzene and propylene dibromide, giving viscosity curves which are abnormal when compared with those of their homologues.

2. The temperature relationships may also be regarded as general and thus independent of the value of the slope, except in the case of the alcohols, which, in this respect, as in that of viscosity at equal slope, are anomalous.

The rest of the memoir is concerned with the discussion of certain general conclusions regarding physicochemical comparisons; and it finally deals with other possible methods of obtaining and comparing viscosity magnitudes.

*Presents, February 22, 1894.*

Transactions.

Adelaide:—Royal Society of South Australia. Transactions.

Vol. XVII. Part. 2. 8vo. *Adelaide* 1893. The Society.

Berlin:—Gesellschaft für Erdkunde. Verhandlungen. Bd. XX.

Nos. 8—10. 8vo. *Berlin* 1893. The Society.

Brisbane:—Royal Society of Queensland. Proceedings. Vol. VI.

Part 1. Vol. VII. Parts 1—2. Vol. VIII. Parts 1—4.

8vo. *Brisbane* 1889–92. The Society.

Calcutta:—Asiatic Society of Bengal. Journal. Vol. LXII. Part 1.

No. 3. Part 2. No. 3. Part 3. Nos. 1—3. 8vo. *Calcutta*

1893; Proceedings. 1893. Nos. 8—9. 8vo. *Calcutta* 1893.

The Society.

Edinburgh:—Royal Society of Edinburgh. Transactions. Vol.

XXXVII. Part 2. 4to. *Edinburgh* 1893; Proceedings.

Vol. XX. Pp. 97—160. 8vo. *Edinburgh* 1893; List of

Members. 1893. 4to.

The Society.